

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C07C 29/80, 29/88	A1	(11) International Publication Number: WO 00/10953
		(43) International Publication Date: 2 March 2000 (02.03.00)

(21) International Application Number: **PCT/US99/18709**

(22) International Filing Date: **18 August 1999 (18.08.99)**

(30) Priority Data:
60/096,939 18 August 1998 (18.08.98) US

(71) Applicant (for all designated States except US): **E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).**

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SUNKARA, Hari, Babu [US/US]; Apartment 43, 5509 Limeric Circle, Wilmington, DE 19808 (US). UMILE, Robert, John, II [US/US]; 1456 Naamans Creek Road, Boothwyn, PA 19061 (US).**

(74) Agent: **SIEGELL, Barbara, C.; E. I. Du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).**

(81) Designated States: **AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**

Published

With international search report.

(54) Title: **PROCESS FOR THE PURIFICATION OF 1,3-PROPANEDIOL**

(57) Abstract

Disclosed is a process for the removal of impurities, especially color forming impurities, from 1,3-propanediol.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AI.	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE

PROCESS FOR THE PURIFICATION OF 1,3-PROPANEDIOL

FIELD OF THE INVENTION

This invention concerns a process for the removal of impurities, especially 5 color forming impurities, from 1,3-propanediol.

TECHNICAL BACKGROUND OF THE INVENTION

1,3-Propanediol is a precursor for polyether glycols, polyester homopolymers and copolymers, and thermoplastic elastomers. The quality of these products is in general dependent on the quality of the raw materials. For 10 some applications, such as fibers, color quality is a major concern. It is known that products derived from 1,3-propanediol have suffered from discoloration. Commercially available samples of 1,3-propanediol starting materials have resulted in brown colored polyether glycols. Disclosed attempts to remove color from the products made from available 1,3-propanediol have been laborious and 15 expensive. Even after extensive purification processes, many products retain a yellow color.

U.S. Patent No. 2,520,733 discloses a process for the purification of polyols prepared from 1,3-propanediol in the presence of acid catalyst (2.5 to 6% by weight) and at a temperature from about 175°C to 200°C. This purification 20 process involves percolation of the polymer through Fuller's earth followed by hydrogenation. Even after this extensive purification process, the final product remains light yellow in color.

U.S. Patent No. 3,326,985 discloses a procedure for the preparation of poly(1,3-propanediol) of molecular weights in the range of 1200-1400 possessing 25 improved color by vacuum stripping, under nitrogen, poly(1,3-propanediol) of lower molecular weight.

U.S. Patent No. 5,659,089 discloses a process for the preparation of poly(2-methyl-1,3-propanediol) by the etherification of 2-methyl-1,3-propanediol. No diol purification process is given. Any available grade of diol can be used in 30 the etherification process.

U.S. Patent No. 5,527,973 discloses a process for providing a purified 1,3 propanediol which can be used as a starting material for low color polyester. That process has several disadvantages including the use of large equipment and the need for dilution with large quantities of water which is difficult to remove from 35 the product.

The process of the present invention alleviates the problem of discolored polymer production in a relatively simple and economical process. The process of the present invention involves purification of, and removal of color precursors

from the starting reactant 1,3-propanediol rather than treating the resulting products. The purified diol from this process is useful for preparing a variety of polymers that include polyether glycols, polyesters and thermoplastic elastomers having excellent color characteristics.

5

SUMMARY OF THE INVENTION

Disclosed is a process for the purification of 1,3-propanediol comprising the steps of

- 10 a) contacting 1,3-propanediol with an acid catalyst at a temperature above that required for impurities to react and below that required for extensive ether formation; and
- b) separating purified 1,3-propanediol from impurities, reacted impurities and the acid catalyst.

DETAILED DESCRIPTION OF THE INVENTION

15 In the preparation of low molecular weight polyether glycols via the dehydration of 1,3-propanediol, polyol quality is an important item. For some applications, such as the production of fibers, color is a major concern. In the past, attempts to prepare polytrimethylene glycols having good color properties have been unsuccessful. This invention discloses a process for the preparation of purified 1,3-propanediol so that products made from it, polyols, polyester 20 homopolymers and copolymers, and thermoplastic elastomers, have excellent color characteristics.

25 Color-free, i.e., chromophore-free, polyether glycols have been prepared from 1,3-propanediol that has been purified of chromophore precursors by a two step process. The first step in the treatment of the diol to free it of color formers (referred to herein as "color precursors") involves the contacting of the 1,3-propanediol with an acid catalyst at elevated temperatures. While not wishing to be bound by any mechanism, applicant believes this step converts color precursors and other impurities to colored and uncolored derivatives that, due to their changed chemical nature, are easily separable from 1,3-propanediol. The 30 second step of the purification process involves the separation of the desirable, purified 1,3-propanediol from the formed colored and uncolored derivatives, from the acid catalyst employed to effect the conversion and, potentially, from residual impurities.

35 An acid catalyst is employed in the treatment process. This acid catalyst promotes the conversion of chromophore precursors to chromophores. The type of acid, (homogeneous or heterogeneous), nature (strong or weak) and the amount of acid catalyst can be varied widely. Although soluble acid catalysts, including inorganic acids and organic sulfonic acids, can be used, heterogeneous acid

catalysts are usually preferred because they can be removed more easily and can easily be recycled. Soluble catalysts, if used, can be removed by extraction or neutralization. Solid heterogeneous acid catalysts can be removed by filtration.

5 Fixed heterogeneous catalyst may also be used, i.e., in a continuous process, provided that contact time is sufficient. Suitable heterogeneous catalysts are perfluorinated ion-exchange polymers (PFIEP) containing pendant sulfonic acid groups or pendant carboxylic acid groups, including Nafion® catalyst, obtainable from the DuPont Company, which is an example of perfluorinated ion-exchange polymers containing pendant sulfonic acid groups, silica or alumina supported 10 Nafion® catalyst, Nafion® Superacid catalyst, a porous nanocomposite of Nafion® resin and silica, acid zeolites, or acid clays.

15 The amount of acid catalyst used herein is not critical, as long as sufficient catalyst is present. Small amounts of catalyst may necessitate extended treatment times. In the case of commercial Nafion® NR50 catalyst, 1% by weight of catalyst versus the weight of 1,3-propanediol was convenient in a batch treatment process. The amount of catalyst employed, in batch treatment processes, will generally be within the range of about 0.1 to 5 wt % based on the amount of 1,3-propanediol used.

20 The temperature for the acid treatment step is selected such that the reaction that converts chromophore precursors readily occurs, but the dehydration reaction of 1,3-propanediol is essentially avoided. The process of the invention is carried out by heating the 1,3-propanediol and the acid catalyst at a temperature within the range of about 100-160°C for 0.1-3 hours under nitrogen atmosphere. At temperature greater than 170°C, the acid can function as a dehydrating catalyst 25 that could lead to the formation of polyether glycols from the 1,3-propanediol. Preferably, the reaction temperature is maintained within the range of 130°C-150°C so that chromophore precursor reaction occurs but essentially no dimers or trimers of 1,3-propanediol are formed.

30 The acid treatment is most conveniently carried out at atmospheric or above atmospheric pressures.

35 In a preferred mode of operation, after the color precursors are transformed, the mixture is cooled to room temperature, and the solid catalyst is removed either by filtration or by decantation. The filtered mixture is then distilled under reduced pressure, and the 1,3-propanediol is collected. The colored impurities and other impurities are left in the distillation flask. The absence of acid catalyst during the vacuum distillation process limits the occurrence of 1,3-propanediol dehydration reactions.

don't have the catalyst present during distillation

The purification of 1,3-propanediol, as described above, can be carried out in either a batch process or a continuous process. The treatment maybe carried out in an agitated system or, if the acid catalyst is in solid form or adhered/attached to a solid support, the treatment may be carried out by passing the diol over or 5 through a bed of the solid acid catalyst.

The process can be conducted as a stand alone process, carried out on available 1,3-propanediol. Alternatively, it may be integrated within a 1,3-propanediol manufacturing process - carried out as one of the steps of a 10 1,3-propanediol manufacturing process. The 1,3-propanediol may be prepared by a variety of manufacturing processes, including the hydration of acrolein followed by hydrogenation of the resulting hydroxypropanal, or the hydroformylation of ethylene oxide followed by reduction of the resulting hydroxypropanal. The 15 purification process may by integrated within either of these or other manufacturing processes.

15 The purified 1,3-propanediol is isolated by means known in the art, most preferably by vacuum distilling the diol away from the converted color precursors and colored and uncolored derivatives.

20 In subsequent processing, the purified diol may be polymerized in the presence of either soluble or insoluble acid catalyst to obtain colorless polyether polyol of low molecular weights. In alternate end uses, the purified diol may be 25 used to prepare polyesters, for example poly(1,3-propylene terephthalate) by methods known in the art.

Depending upon the intensity of the color of the samples to be measured, two different color scales are used. For light colored products, Platinum-Cobalt 25 (APHA) Standard and for dark colored products Gardner Standard are used.

EXAMPLES

EXAMPLE 1

Purification process of 1,3-propanediol using Nafion® acid catalyst

30 A 5 L-three necked flask equipped with a distillation column, mechanical stirrer and nitrogen inlet was charged with 1,3-propanediol (3714.2 g) (commercial grade, Degussa) and Nafion® NR50 catalyst (37.147 g)(DuPont). The mixture was stirred mechanically and heated to 130°C under nitrogen atmosphere. At this temperature, the liquid turned yellow. The liquid then turned brown as it was heated to 150°C. The temperature was kept constant at 150°C for 35 about 2 hours and then allowed to cool to room temperature. No distillate was collected at the receiver flask indicating that essentially no dehydration reaction occurred under these conditions. The solid acid catalyst was removed by decanting the colored solution. Then, the diol was isolated from the colored

impurities by distilling at 100°C under reduced pressure. The APHA color values as measured on a HunterLab ColorQuest (Hunter Associates Laboratory, Inc., Reston, VA) for the purified diol and the original diol are 3 and 7 respectively, indicating an improvement in color characteristics of the purified diol.

5 Heating the thus purified 1,3-propanediol to reflux, under nitrogen, for 3 hours caused the APHA color to increase from 3 to 20. Similar treatment of the starting 1,3-propanediol gave a colored product having APHA color of 60 (i.e., a change from 7 to 60 APHA color). Example 2, below, and comparative example 1, wherein these two samples of 1,3-propanediol are converted to 10 poly(1,3-propanediol) further illustrate the efficacy of the process of the present invention in removing color forming impurities.

EXAMPLE 2

Synthesis of poly(1,3-propanediol) from purified 1,3-propanediol

To a 250 mL three-necked flask, 152.2 g (2.0 mol) of purified 15 1,3-propanediol, prepared as in Example 1, and 1.903 g (10 mmol) of p-toluenesulfonic acid (Aldrich Chemical Co, Milwaukee, WI) were added at room temperature. The mixture was stirred and heated to 180-200°C under nitrogen atmosphere. The distillate (33.1 mL), mostly water was collected as the dehydration reaction progress. The reaction was stopped after 5.5 hours and the 20 mixture was cooled to room temperature. Colorless poly(1,3-propanediol) was obtained from this process. The APHA color value for the polyol was measured and had a value of 48.

COMPARATIVE EXAMPLE 1

Synthesis of poly(1,3-propanediol) from unpurified 1,3-propanediol

25 To 152.2 g (2.0 mol) of 1,3-propanediol (commercial grade, Degussa), 1.903 g (10 mmol) of p-toluenesulfonic acid was added. The mixture was stirred and heated under nitrogen atmosphere. As the temperature of the reaction mixture increased, the color formation was observed at the temperature of 130°C and then the dehydration reaction occurred at 180-200°C. About 32.5 mL of distillate was 30 collected during the dehydration reaction which continued for a time period of 5.5 hours. The color properties of the polyol was measured and had a APHA color value of >300, i.e., off the APHA color scale. The color was measured in Gardner units using a Hellige Daylite Comparator Illuminator (Hellige, Inc., Garden City, NY) which gave a Gardner value of 4.

35 EXAMPLE 3

A Larger Scale Diol Purification

The 1,3-propanediol purification process described in Example 1 was scaled up. A 30-gallon glass-lined clave was charged with polymer grade

WO 00/10953

1,3-propanediol (176 lb) and Nafion® NR50 catalyst (1.76 lb). The mixture was stirred mechanically and heated to 150°C under nitrogen atmosphere. The temperature was kept constant at 150°C for about two hours and then allowed to cool to room temperature. After cooling, the clave was discharged through a filter to recover the solid acid catalyst. The discolored diol solution, that has an APHA color value greater than 300, was distilled in batches using a 22 L-three necked flask equipped with a distillation column, mechanical stirrer and nitrogen inlet at 120°C under reduced pressure. After the distillation was complete the purified diol (144 lb), has an APHA color value of 3. Heating the thus purified 1,3-propanediol to reflux, under nitrogen for 3 hours caused the APHA color value to increase from 3 to 12. As described in Example 2, poly(1,3-propanediol) was made with the purified diol and the APHA color value of the polymer was 30.

CLAIMS

1. A process for the purification of 1,3-propanediol comprising the steps of
 - 5 a) contacting 1,3-propanediol with an acid catalyst at a temperature above that required for impurities to react and below that required for extensive ether formation; and
 - b) isolating purified 1,3-propanediol from impurities, reacted impurities and the acid catalyst.
- 10 2. The process of Claim 1 wherein the purified 1,3-propanediol is isolated by 1) separating the acid catalyst and 2) distilling 1,3-propanediol from the impurities and reacted impurities.
- 15 3. The process of Claim 1 wherein the temperature in step a is between 100 and 160°C.
4. The process of Claim 3 wherein the temperature in step a is between 130 and 150°C.
- 15 5. The process of Claim 1 wherein the acid catalyst is insoluble in 1,3-propanediol acid.
6. The process of Claim 5 wherein the acid catalyst is a solid.
7. The process of Claim 6 wherein the solid acid catalyst is selected from the group consisting of perfluorinated ion-exchange polymers (PFIEP) containing pendant sulfonic acid groups or pendant carboxylic acid groups, acid zeolites, and acid clays.
- 20 8. The process of Claim 7 wherein the solid acid catalyst is selected from the group consisting of perfluorinated ion-exchange polymers containing pendant sulfonic acid groups, silica or alumina supported perfluorinated ion-exchange polymers containing pendant sulfonic acid groups and porous nanocomposites of perfluorinated ion-exchange polymers containing pendant sulfonic acid groups and silica.
- 25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/18709

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5527973	A 18-06-1996	AU 695303 B		13-08-1998
		AU 4432596 A		03-07-1996
		BR 9510012 A		28-10-1997
		CA 2207557 A		20-06-1996
		CN 1170399 A		14-01-1998
		DE 69508112 D		08-04-1999
		DE 69508112 T		12-08-1999
		WO 9618596 A		20-06-1996
		EP 0797561 A		01-10-1997
		ES 2128114 T		01-05-1999
		JP 11509828 T		31-08-1999
		NO 972748 A		13-06-1997
<hr/>				
US 5008473	A 16-04-1991	DE 3632397 A		31-03-1988
		CA 1297912 A		24-03-1992
		DE 3772307 A		26-09-1991
		EP 0261554 A		30-03-1988
		JP 1020135 B		14-04-1989
		JP 1554438 C		23-04-1990
		JP 63091338 A		22-04-1988
<hr/>				
US 5194159	A 16-03-1993	US 5034134 A		23-07-1991
		US 5102549 A		07-04-1992
		AT 128958 T		15-10-1995
		AU 639870 B		05-08-1993
		AU 7159891 A		24-07-1991
		CA 2048624 A		28-06-1991
		DE 69022983 D		16-11-1995
		DE 69022983 T		15-05-1996
		EP 0460196 A		11-12-1991
		JP 7025710 B		22-03-1995
		JP 4505021 T		03-09-1992
		KR 9508888 B		09-08-1995
		WO 9109828 A		11-07-1992
		AU 4139593 A		16-09-1993
		AU 640457 B		26-08-1993
		AU 7205691 A		20-08-1992
		CA 2037215 A,C		15-08-1992
		EP 0498969 A		19-08-1992
		JP 2524545 B		14-08-1996
		JP 4266838 A		22-09-1992
		KR 9602593 B		23-02-1996
<hr/>				

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C07C29/80 C07C29/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 527 973 A (D.R KELSEY) 18 June 1996 (1996-06-18) cited in the application the whole document ---	1
A	US 5 008 473 A (N. BREITKOPF, ET AL.) 16 April 1991 (1991-04-16) the whole document ---	1
A	US 5 194 159 A (K.F. GEORGE, ET AL.) 16 March 1993 (1993-03-16) the whole document -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

'Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

15 November 1999

26/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

English, R